

(19)

Europäisches Patentamt

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(11) EP 0 932 635 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
11.07.2001 Bulletin 2001/28

(51) Int Cl.7: C08G 59/42, C08G 59/14,
C08G 63/676, G02B 1/04

(21) Application number: 97913155.4

(86) International application number:
PCT/EP97/05738

(22) Date of filing: 17.10.1997

(87) International publication number:
WO 98/17704 (30.04.1998 Gazette 1998/17)

(54) CROSSLINKABLE POLYMERS

VERNETZBARE POLYMERE

POLYMERES POUVANT SE RETICULER

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE

(30) Priority: 21.10.1996 EP 96810700

(43) Date of publication of application:
04.08.1999 Bulletin 1999/31

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- ATSUSHI KAMEYAMA ET AL.: "Synthesis of reactive polyesters by a regioselective addition reaction of diepoxides with diacylchlorides and their chemical modification" MACROMOLECULES, vol. 25, no. 9, 27 April 1992, EASTON US, pages 2307-2311, XP000266489 cited in the application

EP 0 932 635 B1

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EP 0 932 635 B1

Description

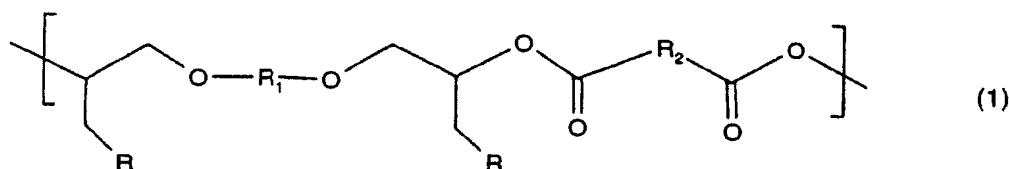
[0001] The present invention relates to novel water-soluble block copolymers comprising polyoxyalkylene units and having crosslinkable side groups, to processes for their preparation, and to their use in the production of mouldings, especially contact lenses.

[0002] Polymers comprising polyalkylene oxide and having polymerisable end groups and their use in the production of contact lenses are already known, for example from EP-A-273 763.

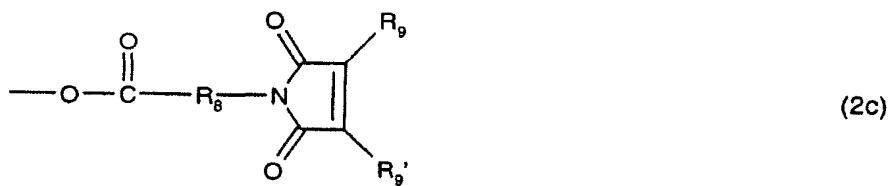
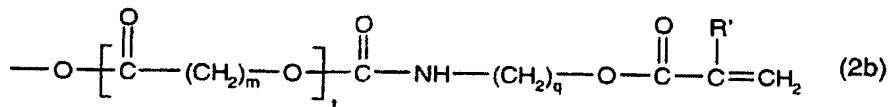
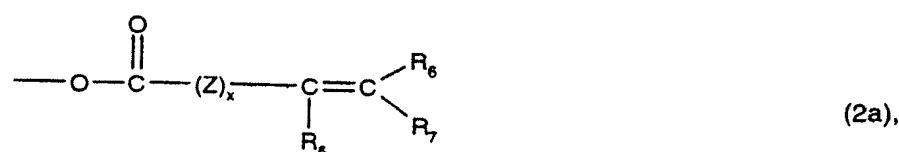
[0003] Furthermore, there are known, for example from A. Kameyama *et al.* Macromol. **25**, 2307 (1992), H. Itoh *et al.* Macromol. **28**, 883 (1995) or H. Itoh *et al.* J. Pol. Sci. A, Pol. Chem. **34**, 217 (1996), polyesters having chloromethyl side groups, polymers derived therefrom that have side groups comprising carboxy groups, and polyesters having vinyl ether side groups.

[0004] Surprisingly, novel crosslinkable polyether-polyester copolymers have now been found, which are suitable especially for the production of contact lenses.

[0005] The present invention relates to prepolymers comprising structural units of the formula



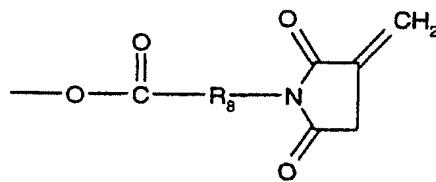
wherein R is a radical



50 or

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EP 0 932 635 B1



10 Z is straight-chained or branched C₁-C₁₂alkylene or unsubstituted or C₁-C₄alkyl- or C₁-C₄-alkoxy-substituted phenylene or C₇-C₁₂aralkylene,
 x and t are each independently of the other the number 0 or 1,
 R₅ is hydrogen, C₁-C₄alkyl or halogen,
 15 R₆ is hydrogen, C₁-C₄alkyl, phenyl, carboxy or halogen,
 R₇ is hydrogen when R₆ is phenyl or carboxy, or is hydrogen or carboxy when R₆ is hydrogen, C₁-C₄alkyl or halogen,
 R₈ is a C₂-C₁₂alkylene radical, a phenylene radical or a C₇-C₁₂aralkylene radical,
 R₉ and R_{9'} are each independently of the other hydrogen, C₁-C₄alkyl or halogen,
 R₁ is a radical of the formula

20 $-\text{[CH}_2\text{-CHR}^*\text{-O}]_n\text{-CH}_2\text{-CHR}^*$ (3a)

or

25 $-\text{[CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O}]_n\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$ (3b);

30 or an alkylene radical having up to 20 carbon atoms which may be interrupted by one or more ester, urethane or ureido groups and/or may be substituted by hydroxy; or a cycloalkylene radical having from 6 to 20 carbon atoms; or an arylen radical having from 6 to 20 carbon atoms; or an arylenealkylene, alkylenearylene, alkylenearylene-alkylene or arylenealkylenearylene radical,
 R₂ is a radical of the formula

35 $-\text{CH}_2\text{-[CH}_2\text{-CHR}^*\text{-O}]_p\text{-CH}_2$ (4)

or or

40 $-\text{R}_3\text{-C(O)-[O-CHR}^*\text{-CH}_2\text{]}_p\text{-O-(O)C-R}_3$ (5);

45 or an alkylene radical having up to 20 carbon atoms which may be interrupted by one or more ester, urethane or ureido groups and/or may be substituted by hydroxy; or a cycloalkylene radical having from 6 to 20 carbon atoms; or an arylen radical having from 6 to 20 carbon atoms; or an arylenealkylene, alkylenearylene, alkylenearylene-alkylene or arylenealkylenearylene radical,
 R', R" and R* are each independently of the others hydrogen or C₁-C₄alkyl,
 R₃ is an alkylene radical having up to 20 carbon atoms; or a cycloalkylene radical having from 6 to 20 carbon atoms; or an arylen radical having from 6 to 20 carbon atoms, and
 50 n, m, p and q are each independently of the others a number from 1 to 30,

with the proviso that at least one of the radicals R₁ and R₂ is a radical of formula (3a), (3b), (4) or (5).

[0006] Z as an alkylene radical is preferably linear or branched C₁-C₈alkylene, especially linear C₁-C₄alkylene and more especially linear C₁-C₂alkylene. In a preferred embodiment of the invention, Z is methylene.

[0007] Z as a phenylene radical is, for example, unsubstituted or methyl- or methoxy-substituted 1,2-, 1,3- or 1,4-phenylene. Z as a phenylene radical is preferably 1,3- or 1,4-phenylene.

[0008] Z as an aralkylene radical is, for example, unsubstituted or methyl- or methoxy-substituted benzylene, the methylene group in each case being bonded to the amine nitrogen. Z as an aralkylene radical is preferably the 1,3- or

EP 0 932 635 B1

1,4-phenylenemethylene radical, the methylene group in each case being bonded to the amine nitrogen -NH-.

[0009] Z is preferably unsubstituted or methyl- or methoxy-substituted phenylene or phenylenemethylene or C₁-C₆alkylene, especially 1,3- or 1,4-phenylene or C₁-C₄alkylene, more especially C₁-C₂alkylene and most especially methylene.

5 [0010] x is preferably the number 0. t is preferably the number 1.

[0011] R₅ is preferably hydrogen, C₁-C₄alkyl or chlorine, especially hydrogen or C₁-C₄alkyl, more especially hydrogen, methyl or ethyl and most especially hydrogen or methyl.

[0012] R₆ is preferably hydrogen, methyl or phenyl and especially hydrogen.

10 [0013] R₇ is preferably hydrogen.

[0014] R₈ is preferably a C₂-C₆alkylene radical or a 1,3- or 1,4-phenylene radical, especially a C₂-C₃alkylene radical. R₉ and R_{9'} are each independently of the other preferably hydrogen, methyl or chlorine. R₉ and R_{9'} are each independently of the other especially hydrogen or methyl.

[0015] Each of R', R" and R' as C₁-C₄alkyl is preferably methyl or ethyl and especially methyl.

15 [0016] R' and R" are each independently of the other preferably hydrogen, methyl or ethyl and especially hydrogen or methyl.

[0017] R' is especially hydrogen or methyl and more especially hydrogen.

[0018] m is preferably a number from 1 to 6 and especially a number from 1 to 4. q is, for example, a number from 1 to 6, preferably a number from 2 to 4 and especially the number 2.

20 [0019] R in formula (1) is preferably a radical of the formula



or

25



30 wherein the variables contained therein each have the meanings and preferred meanings indicated above.

[0020] In an especially preferred embodiment of the invention, R in formula (1) is a radical of formula (2a') indicated above wherein R₅ is hydrogen or methyl.

[0021] In formulae (3a) and (3b), n is, for example, a number from 5 to 30, advantageously from 5 to 25, preferably from 8 to 25 and especially from 10 to 25.

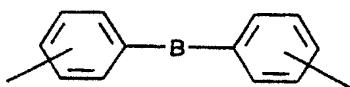
35 [0022] When R₁ is an alkylene radical it is, for example, straight-chained or branched C₁-C₂₀-alkylene which is unsubstituted or substituted, for example by hydroxy, and/or, with the exception of methylene, may be interrupted by one or more groups -COO-, -OCO-, -NHCO-O-, -OCONH- or -NHCONH-. R₁ as an alkylene radical is preferably unsubstituted or hydroxy-substituted C₁-C₂₀alkylene, especially unsubstituted C₁-C₁₂alkylene and more especially unsubstituted C₁-C₆alkylene. Examples of alkylene radicals R₁ that are very especially preferred are methylene, 1,2-ethylene, 1,3-propylene and 1,4-butylene.

40 [0023] R₁ as cycloalkylene is, for example, 1,2-, 1,3- or 1,4-cyclohexylene which may be substituted by C₁-C₄alkylene, or is a radical of the formula



45 R₁ as arylene is, for example, 1,2-, 1,3- or 1,4-phenylene which is unsubstituted or is substituted by C₁-C₄alkyl, C₁-C₄alkoxy or by halogen, or is a radical of the formula

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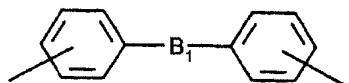
wherein B is, for example, a group -O-, -NH-, -OCO-, -CONH- or -NHCONH-. R₁ as arylene is preferably 1,2-, 1,3- or

EP 0 932 635 B1

1,4-phenylene.

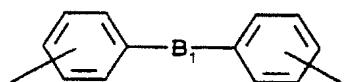
[0024] R_1 as arylenealkylene, alkylenearylene or alkylenearylenealkylene is, for example, a radical $-C_6H_5-C_1-C_4alkylene-, -C_1-C_4alkylene-C_6H_5-$ or $-C_1-C_4alkylene-C_6H_5-C_1-C_4alkylene$, preferably the radical $-C_6H_5-CH_2-, -CH_2-C_6H_5-$ or $-CH_2-C_6H_5-CH_2-$.

5 [0025] R_1 as arylenealkylenearylene is, for example, a radical of the formula



wherein B_1 is straight-chained or branched $C_1-C_6alkylene$ which is unsubstituted or is substituted by hydroxy, preferably straight-chained or branched $C_1-C_4alkylene$. Examples of suitable radicals B_1 are $-CH_2-, -C(CH_3)_2-$ and $-CH_2-CH_2-$.

15 [0026] R_1 is advantageously a radical of formula (3a) or (3b) indicated above, or $C_1-C_{20}alkylene$, 1,2-, 1,3- or 1,4-phenylene or a radical of the formula



wherein B_1 is straight-chained or branched $C_1-C_4alkylene$.

25 [0027] R_1 is preferably a radical of formula (3a) indicated above, or $C_1-C_{20}alkylene$, especially a radical of formula (3a) indicated above wherein n is a number from 5 to 25 and R^* is hydrogen or methyl, or $C_1-C_{12}alkylene$, and more especially a radical of formula (3a) indicated above wherein n is a number from 8 to 25 and R^* is hydrogen or methyl, or $C_1-C_6-alkylene$.

[0028] In formulae (4) and (5), p is preferably a number from 5 to 25, especially from 8 to 25 and more especially from 10 to 25.

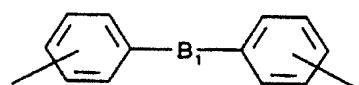
30 [0029] R_3 as an alkylene radical is preferably straight-chained or branched $C_1-C_{12}alkylene$, especially straight-chained or branched $C_1-C_6alkylene$ and more especially straight-chained or branched $C_1-C_4alkylene$. Examples of alkylene radicals R_4 that are very especially preferred are methylene, 1,2-ethylene, 1,3-propylene and 1,4-butylene.

[0030] When R_3 is a cycloalkylene or arylene radical, the definitions and preferred meanings mentioned above for R_2 apply independently.

[0031] R_3 is preferably a straight-chained $C_1-C_4alkylene$ radical.

35 [0032] When R_2 is an alkylene, cycloalkylene, arylene, arylenealkylene, alkylenearylene, alkylenearylenealkylene or arylenealkylenearylene radical, the definitions and preferred meanings given above for R_1 apply independently.

[0033] R_2 is preferably a radical of formula (4) or (5) indicated above, or $C_1-C_{20}alkylene$, 1,2-, 1,3- or 1,4-phenylene or a radical of the formula



45 wherein B_1 is straight-chained or branched $C_1-C_4alkylene$.

[0034] R_2 is especially a radical of formula (4) indicated above, or $C_1-C_{20}alkylene$, more especially a radical of formula (4) indicated above wherein p is a number from 5 to 25 and R^* is hydrogen or methyl, or $C_1-C_{12}alkylene$, and most especially a radical of formula (4) indicated above wherein p is a number from 8 to 25 and R^* is hydrogen, or $C_1-C_6alkylene$.

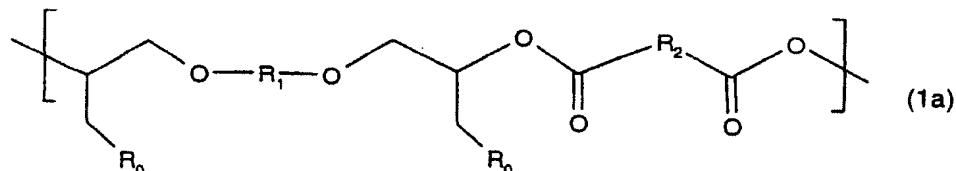
[0035] A preferred embodiment of the present invention relates to prepolymers comprising structural units of formula (1) indicated above wherein R_1 is a radical of formula (3a) indicated above and R_2 is a $C_1-C_{20}alkylene$ radical. Special preference is given to such polymers in which R_1 is a radical of formula (3a) indicated above wherein n is a number from 5 to 25 and R^* is hydrogen or methyl, and R_2 is $C_1-C_6alkylene$.

55 [0036] Another preferred embodiment of the present invention relates to prepolymers comprising structural units of formula (1) indicated above wherein R_1 is a $C_1-C_{20}alkylene$ radical and R_2 is a radical of formula (4) indicated above. Special preference is given to such polymers in which R_1 is $C_1-C_6alkylene$ and R_2 is a radical of formula (4) indicated above wherein p is a number from 5 to 25 and R^* is hydrogen.

EP 0 932 635 B1

[0037] Another preferred embodiment of the present invention relates to prepolymers comprising structural units of formula (1) indicated above wherein the above-mentioned definitions and preferred meanings apply to each of R_1 and R_2 , and R is the acrylate or methacrylate radical $-\text{O}(\text{O})\text{C}-\text{CH}=\text{CH}_2$ or $-\text{O}(\text{O})\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$.

5 [0038] In addition to the structural units of formula (1) mentioned above, the prepolymers of the invention may comprise, for example, structural units of the formula



15 wherein R_0 is halogen or a radical $-\text{O}(\text{O})\text{C}-R_4$ and R_4 is $\text{C}_1\text{-C}_{20}\text{alkyl}$, $\text{C}_6\text{-C}_{20}\text{cycloalkylene}$, $\text{C}_6\text{-C}_{20}\text{arylene}$ or $\text{C}_7\text{-C}_{12}\text{aralkylene}$.

[0039] When R_0 is halogen, it may be, for example, fluorine, bromine, iodine or, especially, chlorine.

20 [0040] R_4 as alkyl is, for example, a straight-chained or branched $\text{C}_1\text{-C}_{20}\text{alkyl}$ radical which is unsubstituted or is substituted by hydroxy, preferably a straight-chained or branched $\text{C}_1\text{-C}_{12}\text{alkyl}$ radical and especially a straight-chained or branched $\text{C}_1\text{-C}_6\text{alkyl}$ radical. Examples are methyl, ethyl, *n*- or iso-propyl, *n*-, iso-, sec- or tert-butyl or straight-chained or branched pentyl or hexyl and, especially, methyl or ethyl.

[0041] R_4 as cycloalkyl is, for example, unsubstituted or $\text{C}_1\text{-C}_4\text{alkyl}$ -substituted cyclohexyl, preferably cyclohexyl which is unsubstituted or is substituted by from 1 to 3 methyl groups, and especially unsubstituted cyclohexyl.

25 [0042] R_4 as aryl is, for example, phenyl which is unsubstituted or is substituted by halogen, hydroxy, carboxy, $\text{C}_1\text{-C}_4\text{alkyl}$ or by $\text{C}_1\text{-C}_4\text{alkoxy}$, preferably phenyl which is unsubstituted or is substituted by chlorine, methyl, methoxy or by carboxy, and especially unsubstituted phenyl.

[0043] R_4 as aralkyl is, for example, phenylmethyl or phenylethyl.

30 [0044] R_4 is preferably $\text{C}_1\text{-C}_{12}\text{alkyl}$, cyclohexyl which is unsubstituted or is substituted by from 1 to 3 methyl groups, phenyl which is unsubstituted or is substituted by chlorine, methyl, methoxy or by carboxy, or phenylmethyl or phenylethyl.

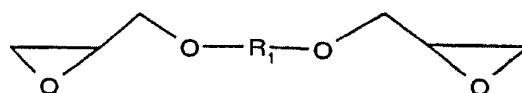
[0045] R_4 is especially $\text{C}_1\text{-C}_6\text{alkyl}$, cyclohexyl or phenyl.

35 [0046] Preferred constituents of the prepolymers of the invention are those units of formula (1a) wherein R_0 is chlorine or a radical $-\text{O}(\text{O})\text{C}-R_4$ and R_4 is $\text{C}_1\text{-C}_6\text{alkyl}$, cyclohexyl or phenyl.

[0047] The crosslinkable prepolymers of the invention comprise, for example, from 100 to 60 mol. % of units of formula (1) and from 0 to 40 mol. % of units of formula (1a). Preference is given to such polymers that comprise from 100 to 80 mol. % of units of formula (1) and from 0 to 20 mol. % of units of formula (1a).

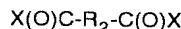
[0048] The crosslinkable prepolymers of the invention can be prepared, for example, by

40 (a) polymerising a compound of the formula



(6)

with a compound of the formula

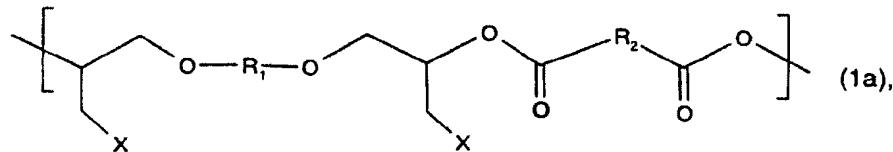


(7)

in the presence of a catalyst, and

55 (b) reacting the polymer obtainable according to (a), which comprises structural units of the formula

EP 0 932 635 B1



10 with a compound of the formula



15 in the presence of a base, R₁ and R₂ each being as defined above, X being halogen, preferably chlorine, and R being a radical of formula (2a), (2c), (2d) or (2b) indicated above wherein t is the number 1.

20 [0049] The compounds of formula (1) wherein R is a radical of formula (2b) and t is the number 0 can be obtained, for example, by converting a polymer of formula (1a) prepared in the manner described above into a corresponding polymer wherein X is hydroxy and reacting the latter with an isocyanate of the formula O=C=N-(CH₂)_q-O-(O)C-CHR'=CH₂ wherein R' and q are as defined above.

25 [0050] The reaction of the diacid dihalide with the diglycidyl compound to form a polyester according to step (a) is known *per se* and can be carried out by methods known *per se*. The reaction of the acid dihalide with the diglycidyl compound is usually carried out in an inert solvent, for example in a higher-boiling alkane or alkane mixture, such as petroleum ether, in a xylene mixture or in toluene, at elevated temperature, for example at from 30 to 120°C, preferably from 40 to 100°C and especially from 60 to 100°C, in the presence of a basic catalyst.

30 [0051] Suitable catalysts are, for example, crown ether complexes, pyridine, quaternary phosphonium salts, tertiary amines or, preferably, quaternary ammonium salts. Examples of suitable catalysts are pyridine, tri-C₁-C₄alkylamines, especially tributylamine, and tetra-C₁-C₄alkyl-ammonium halides, especially tetrabutylammonium halides, such as tetrabutylammonium chloride, tetrabutylammonium iodide or, especially, tetrabutylammonium bromide.

35 [0052] The catalyst is used in the polymerisation reaction, for example, in a molar ratio of from 1:10 to 1:50, preferably from 1:15 to 1:30 and especially of about 1:20, in each case based on the diacid dihalide. The molar ratio of diglycidyl compound to diacid dihalide can vary, for example, from 0.5:1 to 2:1 and is preferably about 1:1.

40 [0053] The reaction of the halide-group-containing polyester obtainable according to (a) with the carboxylic acid of formula (8) is advantageously carried out at elevated temperature, for example at from 30 to 100°C, preferably from 40 to 100°C and especially from 60 to 90°C, in an aprotic-dipolar solvent, for example in DMSO, in the presence of a base, 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU) having proved especially advantageous. The acid is used in a molar excess, based on the halide-group-containing polymer, and the base is advantageously present in about equimolar amounts, based on the acid of formula (8).

45 [0054] Depending on the chosen stoichiometric ratios and reaction conditions, the prepolymer of the invention obtainable after isolation in customary manner consists essentially of structural units of formula (1) indicated above or comprises, in addition to the structural units of formula (1), structural units of formula (1a) indicated above wherein R₀ is halogen. If step (b) is carried out using a mixture of an acid of formula (8) indicated above and an acid of the formula



50 wherein R₄ is as defined above, the prepolymer comprises a mixture of structural units of formula (1), structural units of formula (1a) wherein R₀ is a radical -O-(O)C-R₄, and, where appropriate, structural units of formula (1a) wherein R₀ is halogen.

55 [0055] The prepolymers of the invention are crosslinkable but are uncrosslinked or at least substantially uncrosslinked; moreover, they are stable, that is to say spontaneous crosslinking by homopolymerisation does not take place.

[0056] The prepolymers of the invention are advantageously liquid or readily meltable or water-soluble; their average molecular weight can vary within wide limits. An average molecular weight of, for example, from 1000 to 20 000 has proved advantageous for the prepolymers of the invention.

[0057] Furthermore, the prepolymers comprising structural units of formula (1) and, where appropriate, (1a) can be purified in a manner known *per se*, for example by precipitation with acetone, dialysis or ultrafiltration, with ultrafiltration

EP 0 932 635 B1

being especially preferred. By means of that purification process it is possible to obtain the prepolymers of the invention in an extremely pure form, for example in the form of solvent-free liquids or melts or in the form of concentrated aqueous solutions that are free or at least substantially free of reaction products, such as salts, and of starting materials or other non-polymeric constituents.

5 [0058] The preferred process for purifying the prepolymers of the invention, ultrafiltration, can be carried out in a manner known *per se*. It is possible to carry out the ultrafiltration repeatedly, for example from two to ten times. Alternatively, the ultrafiltration can be carried out continuously until the desired degree of purity has been achieved. The degree of purity can in principle be as high as desired and is preferably so adjusted that the content of undesirable constituents in the prepolymers is, for example, $\leq 0.001\%$, especially $\leq 0.0001\%$ (1 ppm). The prepolymers may, for 10 example depending on their synthesis, comprise in addition constituents that are acceptable from a physiological point of view, for example sodium chloride, such constituents advantageously being present in an amount of $\leq 1\%$, preferably $\leq 0.1\%$ and especially $\leq 0.01\%$.

15 [0059] As has already been mentioned above, the prepolymers of the invention comprising structural units of formula (1) and, where appropriate, (1a) are crosslinkable in an extremely effective and specific manner, especially by means of photocrosslinking.

20 [0060] Accordingly, the present invention relates also to a polymer that can be obtained by photocrosslinking a prepolymer comprising units of formula (1) and, where appropriate, (1a), in the absence or presence of an additional vinyl comonomer. Those crosslinked polymers are insoluble in water.

25 [0061] In the photocrosslinking, a photoinitiator capable of initiating radical crosslinking is suitably added. Examples thereof are known to the person skilled in the art, but there may be mentioned specifically as suitable photoinitiators benzoin methyl ether, 1-hydroxycyclohexyl phenyl ketone, Darocure 1173 or Irgacure types. Crosslinking can then be induced by actinic radiation, for example UV light, or ionising radiation, for example gamma radiation or X-rays.

30 [0062] Photopolymerisation can be carried out without the addition of a solvent, for example when the prepolymer is liquid or readily meltable, or takes place in a suitable solvent. Suitable solvents are in principle any solvents that dissolve the polymers of the invention and the vinyl comonomers that may additionally be used, for example water, alcohols, such as lower alkanols, for example ethanol or methanol, also carboxylic acid amides, such as dimethylformamide, or dimethyl sulfoxide, as well as mixtures of suitable solvents, for example mixtures of water with an alcohol, for example a water/ethanol or water/methanol mixture.

35 [0063] Photocrosslinking is preferably carried out without a solvent or substantially without a solvent or directly from an aqueous solution of the prepolymers of the invention (which solution can be obtained as a result of the preferred purification step, ultrafiltration), where appropriate after the addition of an additional vinyl comonomer. For example, photocrosslinking of an approximately 15 to 90 % strength aqueous solution can be carried out.

40 [0064] The process for the preparation of the crosslinked polymers of the invention comprises, for example, photocrosslinking a prepolymer comprising units of formula (1) and, where appropriate, (1a), especially in substantially pure form, that is to say, for example, after ultrafiltration once or several times, without a solvent or substantially without a solvent or in solution, especially in an aqueous solution, in the absence or presence of an additional vinyl comonomer.

45 [0065] The vinyl comonomer that may additionally be used according to the invention in the photocrosslinking may be hydrophilic, hydrophobic or a mixture of a hydrophobic and a hydrophilic vinyl monomer. Suitable vinyl monomers include especially those which are customarily used in the production of contact lenses. A hydrophilic vinyl monomer is understood as being a monomer that, as a homopolymer, typically yields a polymer that is water-soluble or can absorb at least 10 % by weight water. By analogy, a hydrophobic vinyl monomer is understood as being a monomer that, as a homopolymer, typically yields a polymer that is insoluble in water and can absorb less than 10 % by weight water.

50 [0066] In general, approximately from 0.01 to 80 units of a typical vinyl comonomer react per unit of formula (1) and, as the case may be, (1a).

55 [0067] The proportion of vinyl comonomers, where used, is preferably from 0.5 to 80 units per unit of formula (1), especially from 1 to 30 units of vinyl comonomer per unit of formula (1) and more especially from 5 to 20 units per unit of formula (1).

[0068] It is further preferred to use a hydrophobic vinyl comonomer or a mixture of a hydrophobic vinyl comonomer and a hydrophilic vinyl comonomer, the mixture containing at least 50 % by weight of a hydrophobic vinyl comonomer. In this manner, the mechanical properties of the polymer can be improved without the water content dropping substantially. In principle, however, both conventional hydrophobic vinyl comonomers and conventional hydrophilic vinyl comonomers are suitable for the copolymerisation with a prepolymer comprising groups of formula (1).

[0069] Suitable hydrophobic vinyl comonomers include the following, this list not being exhaustive: C_1 - C_{18} alkyl acrylates and methacrylates, C_3 - C_{18} alkyl-acrylamides and -methacrylamides, acrylonitrile, methacrylonitrile, vinyl C_1 - C_{18} alkanoates, C_2 - C_{18} alkenes, C_2 - C_{18} haloalkenes, styrene, C_1 - C_6 alkylstyrene, vinyl alkyl ethers in which the alkyl moiety has from 1 to 6 carbon atoms, C_2 - C_{10} perfluoroalkyl acrylates and methacrylates or correspondingly partially fluorinated acrylates and methacrylates, C_3 - C_{12} perfluoroalkyl-ethyl-thiocarbonylaminooethyl acrylates and methac-

EP 0 932 635 B1

ylates, acryloxy- and methacryloxy-alkylsiloxanes, N-vinylcarbazole, C₁-C₁₂alkyl esters of maleic acid, fumaric acid, itaconic acid, mesaconic acid and the like. Preference is given, for example, to C₁-C₄alkyl esters of vinylically unsaturated carboxylic acids having from 3 to 5 carbon atoms or vinyl esters of carboxylic acids having up to 5 carbon atoms.

[0070] Examples of suitable hydrophobic vinyl comonomers include methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, styrene, chloroprene, vinyl chloride, vinylidene chloride, acrylonitrile, 1-butene, butadiene, methacrylonitrile, vinyltoluene, vinyl ethyl ether, perfluorohexylethylthiocarbonylaminoethyl methacrylate, isobornyl methacrylate, trifluoroethyl methacrylate, hexafluoroisopropyl methacrylate, hexafluorobutyl methacrylate, tris-trimethylsilyloxy-silyl-propyl methacrylate, 3-methacryloxypropylpentamethyldisiloxane and bis(methacryloxypropyl)tetramethyldisiloxane.

[0071] Suitable hydrophilic vinyl comonomers include the following, this list not being exhaustive: hydroxy-substituted lower alkyl acrylates and methacrylates, acrylamide, methacrylamide, lower alkyl acrylamides and methacrylamides, ethoxylated acrylates and methacrylates, hydroxy-substituted lower alkyl-acrylamides and -methacrylamides, hydroxy-substituted lower alkyl vinyl ethers, sodium ethylenesulfonate, sodium styrenesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, N-vinylpyrrole, N-vinylsuccinimide, N-vinylpyrrolidone, 2- or 4-vinylpyridine, acrylic acid, methacrylic acid, amino- (the term "amino" also including quaternary ammonium), mono-lower alkylamino- or di-lower alkylamino-lower alkyl acrylates and methacrylates, allyl alcohol and the like. Preference is given, for example, to hydroxy-substituted C₂-C₄alkyl (meth)acrylates, five- to seven-membered N-vinylactams, N,N-di-C₁-C₄alkyl (meth)acrylamides, and vinylically unsaturated carboxylic acids having a total of from 3 to 5 carbon atoms.

[0072] Examples of suitable hydrophilic vinyl comonomers include hydroxyethyl methacrylate, hydroxyethyl acrylate, acrylamide, methacrylamide, di-nethylacrylamide, allyl alcohol, vinylpyridine, vinylpyrrolidone, glycerol methacrylate, N-(1,1-dimethyl-3-oxobutyl)acrylamide and the like.

[0073] Preferred hydrophobic vinyl comonomers are methyl methacrylate and vinyl acetate.

[0074] Preferred hydrophilic vinyl comonomers are 2-hydroxyethyl methacrylate, N-vinyl-pyrrolidone and acrylamide.

[0075] The prepolymers of the invention can be processed in a manner known *per se* to form mouldings, especially contact lenses, for example by carrying out the photocrosslinking of the prepolymers of the invention in a suitable contact lens mould. Accordingly, the invention relates also to mouldings consisting essentially of a prepolymer of the invention. Other examples of mouldings of the invention, in addition to contact lenses, are biomedical mouldings and, especially, ophthalmic mouldings, for example intraocular lenses, eye dressings, mouldings for use in surgery, such as heart valves, artificial arteries or the like, and also films or membranes, for example membranes for controlling diffusion, photostructurable foils for information storage, or photoresist materials, for example membranes or mouldings for etching resist or screen printing resist.

[0076] A preferred process for the production of mouldings comprises the following steps:

- 35 a) introducing into a mould a prepolymer comprising structural units of formula (1) and, where appropriate, (1a) that is liquid at room temperature or is readily meltable and is substantially free of solvents, in the absence or presence of an additional vinyl comonomer and/or photoinitiator,
- b) inducing the photocrosslinking,
- c) opening the mould so that the moulding can be removed from the mould.

[0077] Another preferred process for the production of mouldings comprises the following steps:

- 45 a) preparing a substantially aqueous solution of a water-soluble prepolymer comprising structural units of formula (1) and, where appropriate, (1a) in the absence or presence of an additional vinyl comonomer and/or photoinitiator,
- b) introducing the resulting solution into a mould,
- c) inducing the photocrosslinking,
- d) opening the mould so that the moulding can be removed from the mould.

[0078] In the preferred processes outlined above it is in each case especially preferred to introduce the prepolymer into the mould in the absence of an additional vinyl comonomer and in the presence of a photoinitiator.

[0079] For the introduction of the prepolymers of the invention into a mould, processes known *per se* can be used, such as, especially, conventional metering in, for example by means of dropwise introduction. If vinyl comonomers are present, the above-mentioned comonomers in the amounts mentioned there are suitable. Vinyl comonomers that may be present are advantageously first mixed with the prepolymer of the invention and then introduced into the mould.

[0080] Appropriate moulds are manufactured, for example, from polypropylene. Suitable materials for reusable moulds are, for example, quartz, sapphire glass or metals.

[0081] When the mouldings to be produced are contact lenses, they can be produced in a manner known *per se*, for example in a conventional "spin-casting mold", as described, for example, in US-A-3 408 429, or by the so-called

EP 0 932 635 B1

full-mold process in a static mould, as described, for example, in US-A-4 347 198.

[0082] The photocrosslinking can be induced in the mould, for example by actinic radiation, e.g. UV light, or ionising radiation, e.g. gamma radiation or X-rays.

5 [0083] As has already been mentioned, the photocrosslinking is advantageously carried out in the presence of a photoinitiator capable of initiating radical crosslinking. The photoinitiator is advantageously added to the prepolymers of the invention before introduction into the mould, preferably by mixing the polymers and the photoinitiator together. The amount of photoinitiator can be chosen within wide limits, an amount of up to 0.05 g/g of polymer and especially of up to 0.003 g/g of polymer having proved advantageous.

10 [0084] It is to be emphasised that according to the invention the crosslinking can be effected in a very short time, for example in < 60 minutes, advantageously in ≤ 20 minutes, preferably in ≤ 10 minutes, especially in ≤ 5 minutes, more especially in ≤ 1 minute and most especially in ≤ 30 seconds.

15 [0085] Opening of the mould so that the moulding can be removed from the mould can be carried out in a manner known *per se*.

20 [0086] When the moulding produced according to the invention is a contact lens and when the latter has been produced without a solvent from a previously purified prepolymer of the invention, then it is generally not necessary, after removing the moulding, to carry out subsequent purification steps, for example extraction. This is because the prepolymers used do not contain any undesirable low-molecular-weight constituents; consequently, the crosslinked product is also free or substantially free of such constituents and subsequent extraction is unnecessary. Accordingly, the contact lens can be converted directly into a ready-to-use contact lens in customary manner by hydration. Suitable forms of hydration, by means of which ready-to-use contact lenses having different water contents are obtainable, are known to the person skilled in the art. The contact lens is swelled, for example, in water, in an aqueous salt solution, especially in an aqueous salt solution having an osmolarity of approximately from 200 to 450 milliosmol in 1000 ml (unit: mOsm/l), preferably approximately from 250 to 350 mOsm/l and especially approximately 300 mOsm/l, or in a mixture of water or an aqueous salt solution with a physiologically tolerable polar organic solvent, for example glycerol. Swelling of the prepolymer in water or in aqueous salt solutions is preferred.

25 [0087] The aqueous salt solutions used for the hydration are advantageously solutions of physiologically tolerable salts, such as buffer salts that are customary in the field of contact lens care, for example phosphate salts, or agents for establishing isotonicity that are customary in the field of contact lens care, such as, especially, alkali metal halides, for example sodium chloride, or solutions of mixtures thereof. An example of an especially suitable salt solution is a synthetic, preferably buffered lachrymal fluid that is adapted to natural lachrymal fluid as regards pH and osmolarity, for example an unbuffered sodium chloride solution, preferably a sodium chloride solution that is buffered, for example buffered with phosphate buffers, and the osmolarity and pH of which correspond to the osmolarity and pH of human lachrymal fluid.

30 [0088] The hydration fluids defined above are preferably pure, that is to say free or substantially free of undesirable constituents. Special preference is given to pure water or to a synthetic lachrymal fluid as described above.

35 [0089] When the moulding produced according to the invention is a contact lens and when the latter has been produced from an aqueous solution of a previously purified prepolymer of the invention, then the crosslinked product does not contain any troublesome impurities either. Subsequent extraction is therefore unnecessary. Since the crosslinking is carried out in a substantially aqueous solution, subsequent hydration is also unnecessary. The contact lenses obtainable according to that process are therefore distinguished, according to an advantageous embodiment, by the fact that they are suitable for their designated use without extraction. In this connection, designated use is understood as meaning especially that the contact lenses can be inserted into the human eye.

40 [0090] The contact lenses obtainable according to the invention have a range of unusual and extremely advantageous properties. Of those properties there may be mentioned, for example, their excellent tolerability by the human cornea, which is based on a balance of water content, oxygen permeability and mechanical properties. Moreover, the contact lenses of the invention exhibit a high degree of dimensional stability. No changes in shape were discernible even after autoclaving at, for example, about 120°C.

45 [0091] It can also be emphasised that the contact lenses of the invention, that is to say especially those comprising a crosslinked polymer of a prepolymer comprising units of formula (1) and, where appropriate, (1a), can be produced in a very simple and efficient manner as compared with the prior art. This is the result of several factors. Firstly, the starting materials are inexpensive to obtain or prepare. Secondly, there is the advantage that the prepolymers are surprisingly stable, so that they can be subjected to a high degree of purification. Accordingly, it is possible to use for the crosslinking a polymer that requires virtually no subsequent purification, such as, especially, the complicated extraction of unpolymerised constituents. Moreover, the crosslinking can be carried out without a solvent or in an aqueous solution, so that the subsequent exchange of solvents or the hydration step, respectively, is not required. Finally, the photopolymerisation takes place in a short time, so that the process for the production of the contact lenses of the invention can be made extraordinarily economical from that point of view also.

50 [0092] All the advantages mentioned above naturally apply not only to contact lenses but also to other mouldings

EP 0 932 635 B1

according to the invention. The sum of the various advantageous aspects in the production of the mouldings of the invention leads to the mouldings of the invention being suitable especially as mass-produced articles, for example as contact lenses that are worn for a short period of time and are then replaced by new lenses.

[0093] In the Examples which follow, unless expressly indicated to the contrary, quantities are by weight and temperatures are given in degrees Celsius. Unless indicated otherwise, molecular weights M_n are determined by means of gel permeation chromatography (GPC) [size exclusion chromatography (SEC)] using DMF as solvent, and are related to the calibration standard of polymethyl methacrylate (PMMA).

Preparation Examples

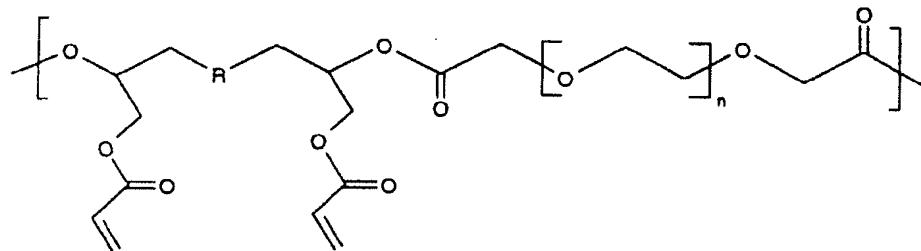
Example 1:

[0094]

(a) 63.7 g of polyethylene glycol 600 diacid dichloride (prepared by reacting polyethylene glycol 600 diacid with thionyl chloride) are dissolved in 500 ml of toluene. 1.6 g of tetrabutylammonium bromide (TBAB) and 20.2 g of diglycidyl ether of butane-1,4-diol are added thereto and the mixture is heated to 90°C, with stirring. When the epoxy groups have reacted completely (which takes about 2 hours), the product is precipitated from tert-butyl methyl ether in the form of a yellow oil.

(b) 25.2 g of the product prepared according to (a) are dissolved in 200 ml of DMSO.

19.5 g of acrylic acid and 41.1 g of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) are added thereto and the mixture is heated to 70°C, with stirring. After 24 hours at that temperature, 300 ml of water are added to the clear brown reaction mixture. The product is extracted with chloroform and the organic phase is washed first with 0.1N hydrochloric acid and then with 5 % strength NaHCO₃ solution. After removal of the solvent, a polymer comprising structural units of the formula



wherein R is the radical $-\text{O}-(\text{CH}_2)_4-\text{O}-$ and n ≈ 14, is obtained in the form of a viscous yellow oil ($M_n = 3000$, $M_w = 4000$).

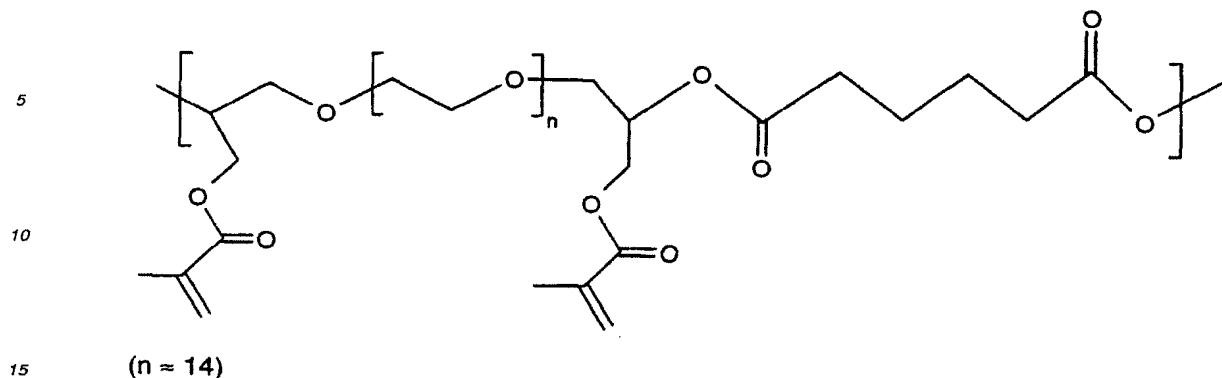
Example 2:

[0095]

(a) 120 g of diglycidyl ether of polyethylene glycol 600 are dissolved in 100 ml of toluene. 3.2 g of TBAB and 36.6 g of adipic acid dichloride are added thereto and the mixture is heated to 90°C, with stirring. When the epoxy groups have reacted completely (which takes about 1 hour), the product is precipitated from tert-butyl methyl ether in the form of a yellow oil.

(b) 23.5 g of the product prepared according to (a) are dissolved in 200 ml of DMSO. 25.8 g of methacrylic acid and 41.1 g of DBU are added thereto and the mixture is heated to 90°C, with stirring. After 24 hours at that temperature, the reaction mixture is diluted with 300 ml of water and the product is then extracted therefrom with chloroform. The organic phase is washed with 0.1N hydrochloric acid and then with 5 % strength NaHCO₃ solution. After removal of the solvent, a polymer comprising structural units of the formula

EP 0 932 635 B1

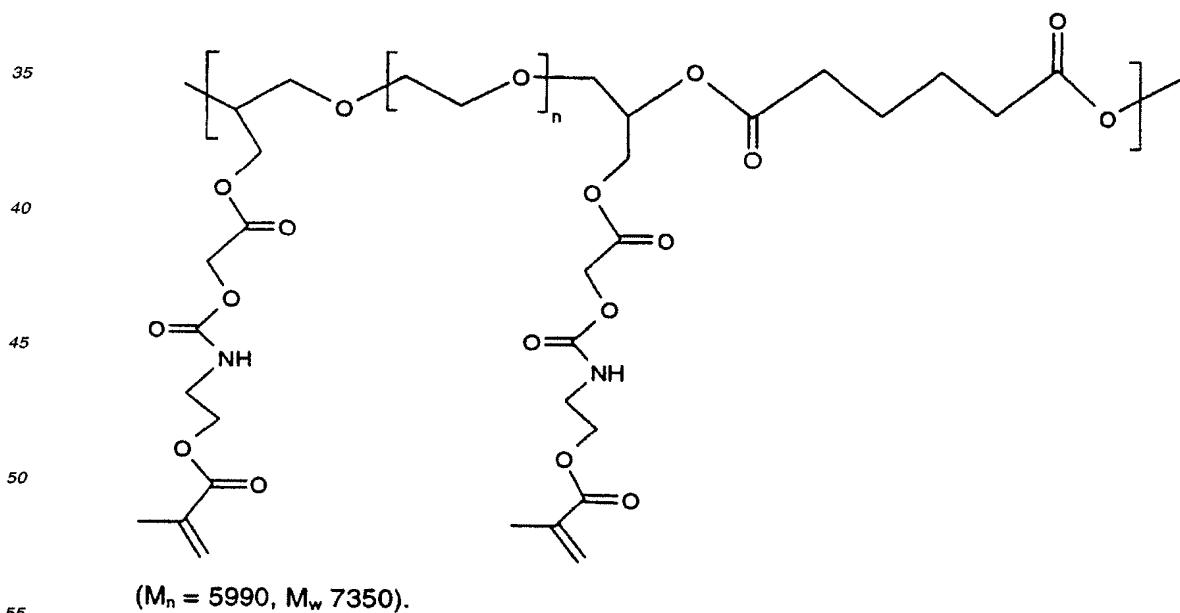


is obtained in the form of a viscous yellow oil ($M_n = 3800$, $M_w = 4900$).

20 [0096] **Example 3:** Reaction of 70 g of diglycidyl ether of polyethylene glycol 1000 with 12.8 g of adipic acid dichloride, with the addition of 1.1 g of TBAB, by the process according to Example 2(a), and reaction of 26.5 g of the resulting product with 17.4 g of methacrylic acid, with the addition of 30.7 g of DBU, according to Example 2(b) yields a polymeric oil comprising structural units of the formula indicated in Example 2 wherein $n = 23$ ($M_n = 3300$, $M_w = 4200$).

25 [0097] **Example 4:** 23.5 g of the product obtained according to Example 2(a) are dissolved in 200 ml of DMSO. 20.6 g of glycolic acid and 41.2 g of DBU are added thereto and the mixture is heated to 90°C, with stirring. After 24 hours at that temperature, the reaction mixture is diluted with 300 ml of water and the product is then extracted therefrom with chloroform.

30 [0098] 23.9 g of the product so prepared are dissolved in 170 ml of dioxane, and 0.18 g of N,N-dimethylcyclohexylamine is added thereto while introducing air. 43 g of isocyanatoethyl methacrylate, dissolved in 40 ml of dioxane, are added dropwise thereto and the mixture is then heated at 80°C for 5 hours. At the end of that time, the product is precipitated from tert-butyl methyl ether, yielding a polymer comprising structural units of the formula



EP 0 932 635 B1

Application Examples

[0099] Example 5: 1.5 mg of Irgacure® 2959 are dissolved in 0.5 g of the polymer obtained according to Example 1. A 0.1 mm thick film is prepared from the clear viscous solution between two glass plates having spacers. The film is irradiated for 1.5 minutes using a Höne lamp. A clear, flexible film is obtained which swells in water to form a clear hydrogel having a water content of 40 %.

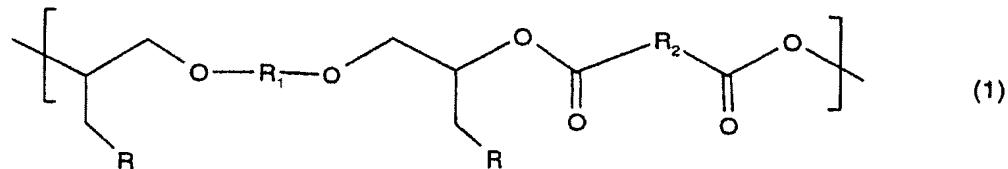
[0100] Example 6: 3 mg of Irgacure® 2959 are dissolved in 1 g of the polymer obtained according to Example 2. A 0.1 mm thick film is prepared from the clear viscous solution between two glass plates having spacers. The film is irradiated for 1.5 minutes using a Hönlé lamp. A clear, flexible film is obtained which swells in water to form a clear hydrogel having a water content of 40 %.

[0101] Example 7: 3 mg of Irgacure® 2959 are dissolved in 1 g of the polymer obtained according to Example 3. A 0.1 mm thick film is prepared from the clear viscous solution between two glass plates having spacers. The film is irradiated for 30 seconds using a Höne lamp. A clear, solid film is obtained.

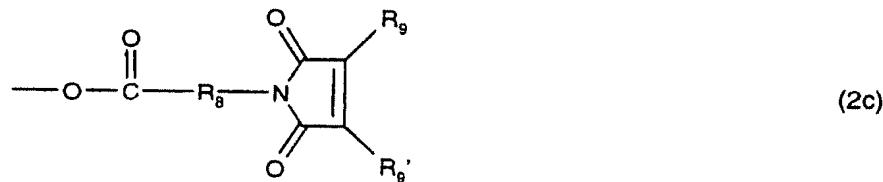
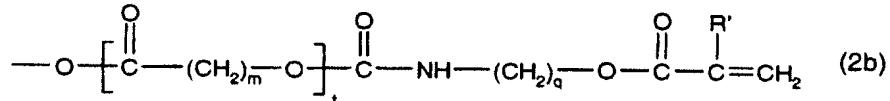
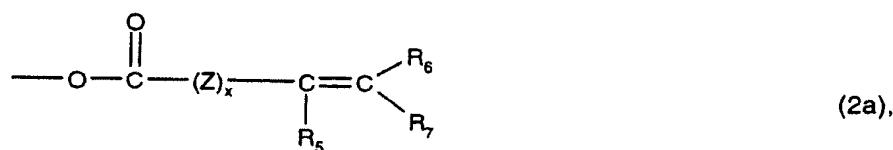
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Claims

1. A prepolymer comprising structural units of the formula

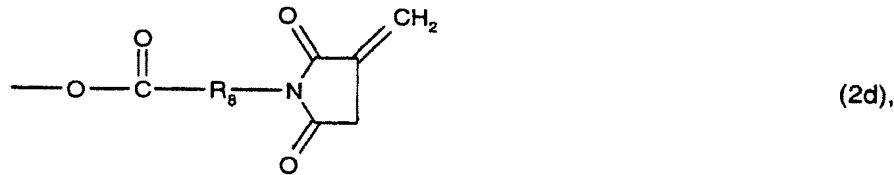


wherein R is a radical



or

EP 0 932 635 B1



10 Z is straight-chained or branched C₁-C₁₂alkylene or unsubstituted or C₁-C₄alkyl- or C₁-C₄-alkoxy-substituted phenylene or C₇-C₁₂aralkylene,
 x and t are each independently of the other the number 0 or 1,
 R₅ is hydrogen, C₁-C₄alkyl or halogen,
 R₆ is hydrogen, C₁-C₄alkyl, phenyl, carboxy or halogen,
 15 R₇ is hydrogen when R₆ is phenyl or carboxy, or is hydrogen or carboxy when R₆ is hydrogen, C₁-C₄alkyl or halogen,
 R₈ is a C₂-C₁₂alkylene radical, a phenylene radical or a C₇-C₁₂aralkylene radical,
 R₉ and R_{9'} are each independently of the other hydrogen, C₁-C₄alkyl or halogen,
 R₁ is a radical of the formula

20

-[CH₂-CHR"-O]_n-CH₂-CHR"- (3a)

25 or

-[CH₂-CH₂-CH₂-CH₂-O]_n-CH₂-CH₂-CH₂-CH₂- (3b);

30 or an alkylene radical having up to 20 carbon atoms which may be interrupted by one or more ester, urethane or ureido groups and/or may be substituted by hydroxy; or a cycloalkylene radical having from 6 to 20 carbon atoms; or an arylene radical having from 6 to 20 carbon atoms; or an arylenealkylene, alkylenearylene, alkylenearylenealkylene or arylenealkylenearylene radical,
 R₂ is a radical of the formula

35

-CH₂-[CH₂-CHR*-O]_p-CH₂- (4)

or

40

-R₃-C(O)-[O-CHR*-CH₂]_p-O-(O)C-R₃- (5);

45 or an alkylene radical having up to 20 carbon atoms which may be interrupted by one or more ester, urethane or ureido groups and/or may be substituted by hydroxy; or a cycloalkylene radical having from 6 to 20 carbon atoms; or an arylene radical having from 6 to 20 carbon atoms; or an arylenealkylene, alkylenearylene, alkylenearylenealkylene or arylenealkylenearylene radical,
 R', R" and R* are each independently of the others hydrogen or C₁-C₄alkyl,
 R₃ is an alkylene radical having up to 20 carbon atoms; or a cycloalkylene radical having from 6 to 20 carbon atoms; or an arylene radical having from 6 to 20 carbon atoms, and
 50 n, m, p and q are each independently of the others a number from 1 to 30,

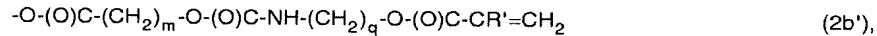
with the proviso that at least one of the radicals R₁ and R₂ is a radical of formula (3a), (3b), (4) or (5).

55 2. A prepolymer according to claim 1, wherein R is a radical of the formula

-O-(O)C-CR₅=CH₂ (2a')

EP 0 932 635 B1

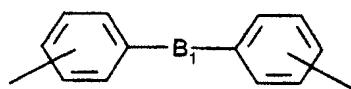
or



R₅ and R' are each independently of the other hydrogen or C₁-C₄alkyl, and m and q are each independently of the other a number from 1 to 30.

10 3. A prepolymer according to claim 2, wherein R is a radical of formula (2a') wherein R₅ is hydrogen or methyl.

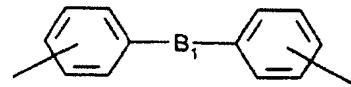
4. A prepolymer according to any one of claims 1 to 3, wherein R₁ is a radical of formula (3a) or (3b) indicated in claim 1, C₁-C₂₀alkylene, 1,2-, 1,3- or 1,4-phenylene, or a radical of the formula



20 wherein B₁ is straight-chained or branched C₁-C₄alkylene.

5 5. A prepolymer according to any one of claims 1 to 4, wherein R₁ is a radical of formula (3a) indicated in claim 1, or is C₁-C₂₀alkylene.

25 6. A prepolymer according to any one of claims 1 to 5, wherein R₂ is a radical of formula (4) or (5) indicated in claim 1, C₁-C₂₀alkylene, 1,2-, 1,3- or 1,4-phenylene, or a radical of the formula



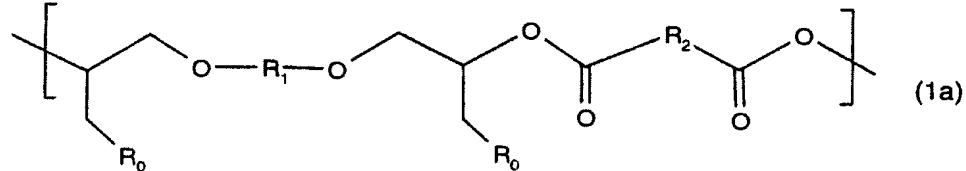
wherein B₁ is straight-chained or branched C₁-C₄alkylene.

35 7. A prepolymer according to any one of claims 1 to 6, wherein R₂ is a radical of formula (4) indicated in claim 1, or is C₁-C₂₀alkylene.

40 8. A prepolymer according to any one of claims 1 to 7, wherein R₁ is a radical of formula (3a) indicated above and R₂ is a C₁-C₂₀alkylene radical.

45 9. A prepolymer according to any one of claims 1 to 7, wherein R₁ is a C₁-C₂₀alkylene radical and R₂ is a radical of formula (4) indicated above.

10. A prepolymer according to any one of claims 1 to 9 which comprises, in addition to the structural units of formula (1), structural units of the formula



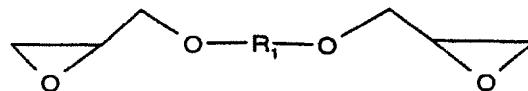
55 wherein R₀ is halogen or a radical -O-(O)C-R₄ and R₄ is C₁-C₂₀alkyl, C₆-C₂₀cycloalkylene, C₆-C₂₀arylene or C₇-C₁₂aralkylene.

EP 0 932 635 B1

11. A prepolymer according to claim 10, wherein R_0 is halogen, preferably chlorine.

12. A process for the preparation of a prepolymer according to claim 1, which comprises

5 (a) polymerising a compound of the formula



(6)

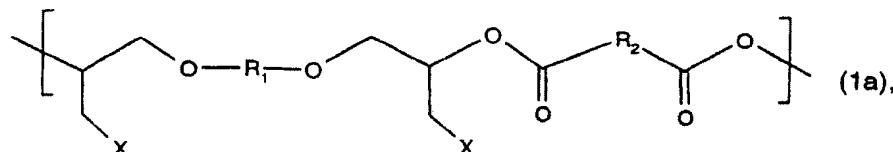
with a compound of the formula



(7)

in the presence of a catalyst, and

20 (b) reacting the polymer obtainable according to (a), which comprises structural units of the formula



(1a),

30 with a compound of the formula



(8)

35 in the presence of a base, R_1 and R_2 each being as defined in claim 1, X being halogen, preferably chlorine, and R being a radical of formula (2a), (2c), (2d) or (2b) indicated in claim 1 wherein t is the number 1.

40 13. A polymer that is obtainable by crosslinking a prepolymer according to any one of claims 1 to 11 in the absence or presence of an additional vinyl comonomer.

45 14. A polymer according to claim 13 that is obtainable by photocrosslinking a prepolymer according to any one of claims 1 to 11 in the absence of an additional vinyl comonomer.

15. A polymer according to claim 13 that is obtainable by photocrosslinking a prepolymer according to any one of claims 1 to 11 in the presence of from 0.5 to 80 units of an additional vinyl comonomer per unit of formula (1), especially from 1 to 30 units of vinyl comonomer per unit of formula (1) and more especially from 5 to 20 units per unit of formula (1).

50 16. A process for the preparation of a polymer according to claim 13, which comprises photocrosslinking a prepolymer according to any one of claims 1 to 11 in the absence or presence of an additional vinyl comonomer.

17. A process according to claim 16, wherein the prepolymer is used in substantially pure form.

55 18. A process for the production of a moulding, which comprises the following steps:

a) introducing into a mould a prepolymer comprising structural units of formula (1) and, where appropriate, (1a) that is liquid at room temperature or is readily meltable and is substantially free of solvents, in the absence

EP 0 932 635 B1

or presence of an additional vinyl comonomer and/or photoinitiator,
 b) inducing the photocrosslinking,
 c) opening the mould so that the moulding can be removed from the mould.

5 19. A process for the production of a moulding, which comprises the following steps:

10 a) preparing a substantially aqueous solution of a water-soluble prepolymer comprising structural units of formula (1) and, where appropriate, (1a) in the absence or presence of an additional vinyl comonomer and/or photoinitiator,
 b) introducing the resulting solution into a mould,
 c) inducing the crosslinking,
 d) opening the mould so that the moulding can be removed from the mould.

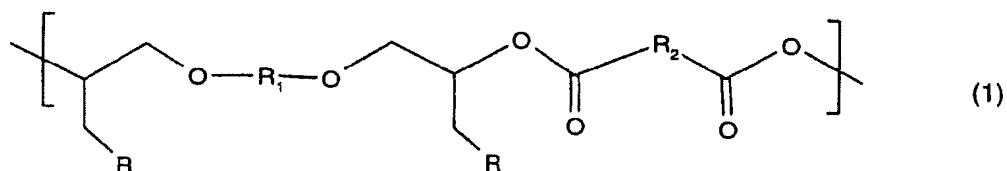
15 20. A process according to either claim 18 or claim 19, wherein the moulding is a contact lens.

21. A moulding, especially a contact lens, that is obtainable by the process according to either claim 18 or claim 19.

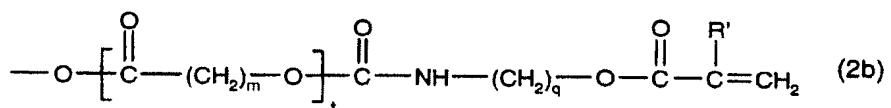
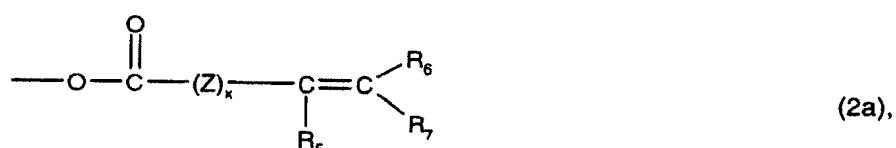
22. A contact lens according to claim 21 that is suitable for its designated use without extraction.

20 Patentansprüche

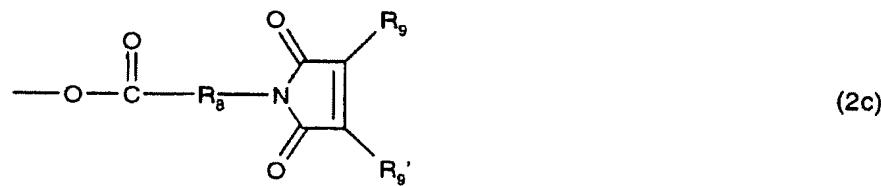
1. Präpolymer, das Struktureinheiten der folgenden Formel umfaßt:



35 worin R für einen Rest:

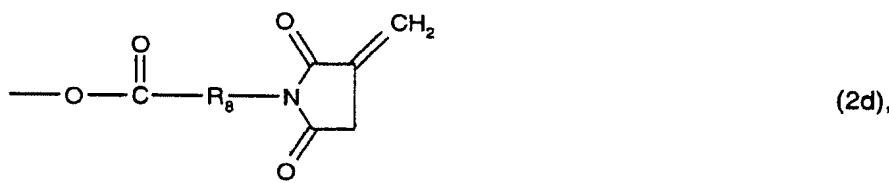


EP 0 932 635 B1



10

oder



20

steht,

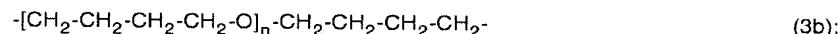
25 Z geradkettiges oder verzweigtes C₁-C₁₂-Alkylen oder nicht substituiertes oder C₁-C₄-alkyl oder C₁-C₄-alkoxy-
substituiertes Phenylen oder C₇-C₁₂-Aralkylen bedeutet,
x und t unabhängig voneinander jeweils eine Zahl 0 oder 1 bedeuten,
R₅ für Wasserstoff, C₁-C₄-Alkyl oder Halogen steht,
R₆ für Wasserstoff, C₁-C₄-Alkyl, Phenyl, Carboxy oder Halogen steht,
R₇ für Wasserstoff steht, wenn R₆ Phenyl oder Carboxy bedeutet, oder für Wasserstoff oder Carboxy steht,
wenn R₆ für Wasserstoff, C₁-C₄-Alkyl oder Halogen steht,
R₈ für einen C₂-C₁₂-Alkylenrest, einen Phenylrest oder einen C₇-C₁₂-Aralkylenrest steht,
R₉ und R_{9'} jeweils unabhängig voneinander für Wasserstoff, C₁-C₄-Alkyl oder Halogen stehen,
R₁ für einen Rest der folgenden Formel:

35



oder

40



45

oder einen Alkylenrest mit bis zu 20 Kohlenstoffatomen, der durch eine oder mehrere Ester-, Urethan- oder Ureidogruppen unterbrochen und/oder durch Hydroxy substituiert sein kann, oder einen Cycloalkylenrest mit 6 bis 20 Kohlenstoffatomen oder einen Arylenrest mit 6 bis 20 Kohlenstoffatomen oder einen Arylenalkylen-, Alkylenarylen-, Alkylenarylenalkylen- oder Arylenalkylenarylenrest steht,
R₂ für einen Rest der folgenden Formel

50



oder

55



oder einen Alkylenrest mit bis zu 20 Kohlenstoffatomen, der durch eine oder mehrere Ester-, Urethan- oder

EP 0 932 635 B1

Ureidogruppen unterbrochen und/oder durch Hydroxy substituiert sein kann, oder einen Cycloalkylenrest mit 6 bis 20 Kohlenstoffatomen oder einen Arylenrest mit 6 bis 20 Kohlenstoffatomen oder einen Arylenalkylen-, Alkylenarylen-, Alkylenarylenalkylen- oder Arylenalkylenarylenrest steht,

5 R', R'' und R* jeweils unabhängig voneinander für Wasserstoff oder C₁-C₄-Alkyl stehen,
R₃ für einen Alkylenrest mit bis zu 20 Kohlenstoffatomen oder einen Cycloalkylenrest mit 6 bis 20 Kohlenstoffatomen oder einen Arylenrest mit 6 bis 20 Kohlenstoffatomen steht und
n, m, p und q jeweils unabhängig voneinander eine Zahl von 1 bis 30 bedeuten,

10 wobei gilt, daß mindestens einer der Reste R₁ und R₂ für einen Rest der Formel (3a), (3b), (4) oder (5) steht.

15 2. Präpolymer nach Anspruch 1, worin R für einen Rest der Formel



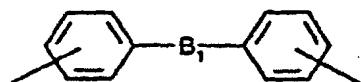
20 oder



25 steht, worin R₅ und R' unabhängig voneinander jeweils für Wasserstoff oder C₁-C₄-Alkyl stehen und m und q unabhängig voneinander jeweils eine Zahl von 1 bis 30 bedeuten.

30 3. Präpolymer nach Anspruch 2, worin der Rest R für einen Rest der Formel (2a') steht, worin R₅ Wasserstoff oder Methyl bedeutet.

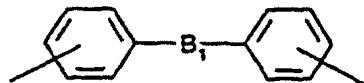
4. Präpolymer nach einem der Ansprüche 1 bis 3, worin R₁ für einen Rest der Formel (3a) oder (3b) gemäß Angabe in Anspruch 1, C₁-C₂₀-Alkylen, 1,2-, 1,3- oder 1,4-Phenylen oder einen Rest der Formel



35 worin B₁ geradkettiges oder verzweigtes C₁-C₄-Alkylen bedeutet, steht.

40 5. Präpolymer nach einem der Ansprüche 1 bis 4, worin R₁ für einen Rest der Formel (3a) gemäß Angabe in Anspruch 1 oder C₁-C₂₀-Alkylen steht.

6. Präpolymer nach einem der Ansprüche 1 bis 5, worin R₂ für einen Rest der Formel (4) oder (5) gemäß Angabe in Anspruch 1, C₁-C₂₀-Alkylen, 1,2-, 1,3- oder 1,4-Phenylen oder einen Rest der Formel



45 50 worin B₁ geradkettiges oder verzweigtes C₁-C₄-Alkylen bedeutet, steht.

7. Präpolymer nach einem der Ansprüche 1 bis 6, worin R₂ für einen Rest der Formel (4) gemäß Angabe in Anspruch 1 oder C₁-C₂₀-Alkylen steht.

8. Präpolymer nach einem der Ansprüche 1 bis 7, worin R₁ für einen Rest der Formel (3a) gemäß obigen Angaben steht und R₂ einen C₁-C₂₀-Alkylenrest bedeutet.

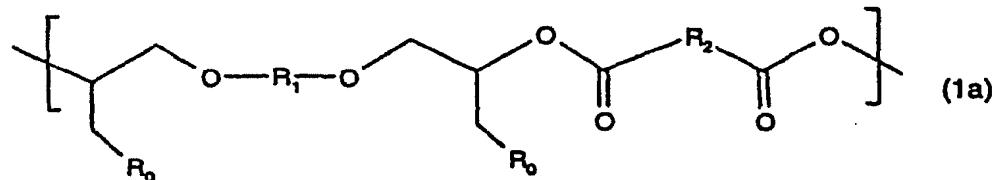
9. Präpolymer nach einem der Ansprüche 1 bis 7, worin R₁ für einen C₁-C₂₀-Alkylenrest steht und R₂ einen Rest der

EP 0 932 635 B1

Formel (4) gemäß obigen Angaben bedeutet.

10. Präpolymer nach einem der Ansprüche 1 bis 9, das neben den Struktureinheiten der Formel (1) Struktureinheiten der folgenden Formel umfaßt:

5



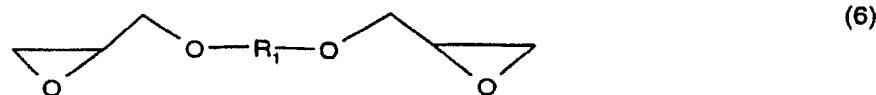
15 worin R_0 für Halogen oder einen Rest $-O-(O)C-R_4$ steht und R_4 für C_1-C_{20} -Alkyl, C_6-C_{20} -Cycloalkylen, C_6-C_{20} -Arylen oder C_7-C_{12} -Aralkylen steht.

11. Präpolymer nach Anspruch 10, worin R_0 für Halogen, vorzugsweise Chlor, steht.

20 12. Verfahren zur Herstellung eines Präpolymers nach Anspruch 1 durch

(a) Polymerisieren einer Verbindung der Formel:

25



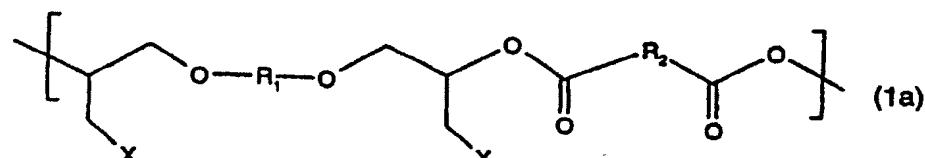
30 mit einer Verbindung der Formel



35 in Gegenwart eines Katalysators und

(b) Umsetzen des gemäß (a) erhältlichen Polymeren, das Struktureinheiten der folgenden Formel umfaßt:

40



45

mit einer Verbindung der Formel



50

in Gegenwart einer Base, wobei R_1 und R_2 jeweils die in Anspruch 1 angegebene Bedeutung besitzen, X für Halogen, vorzugsweise Chlor, steht und R für einen Rest der Formeln (2a), (2c), (2d) oder (2b) gemäß Angaben in Anspruch 1 steht, wobei t die Zahl 1 bedeutet.

55 13. Polymer, erhältlich durch Vernetzen eines Präpolymers nach einem der Ansprüche 1 bis 11 in Abwesenheit oder Gegenwart eines weiteren Vinylcomonomers.

EP 0 932 635 B1

14. Polymer nach Anspruch 13, erhältlich durch Photovernetzen eines Präpolymers gemäß einem der Ansprüche 1 bis 11 in Abwesenheit eines weiteren Vinylcomonomers.

5 15. Polymer nach Anspruch 13, erhältlich durch Photovernetzen eines Präpolymers nach einem der Ansprüche 1 bis 11 in Gegenwart von 0,5 bis 80 Einheiten eines weiteren Vinylcomonomers pro Einheit der Formel (1), insbesondere von 1 bis 30 Einheiten eines Vinylcomonomers pro Einheit der Formel (1) und insbesondere von 5 bis 20 Einheiten pro Einheit der Formel (1).

10 16. Verfahren zur Herstellung eines Polymers nach Anspruch 13 durch Photovernetzen eines Präpolymers gemäß einem der Ansprüche 1 bis 11 in Abwesenheit oder Gegenwart eines weiteren Vinylcomonomers.

17. Verfahren nach Anspruch 16, wobei das Präpolymer in einer im wesentlichen reinen Form verwendet wird.

15 18. Verfahren zur Herstellung eines Formteils, das die folgenden Stufen umfaßt:

(a) Einbringen eines Präpolymers, das Struktureinheiten der Formel (1) und - falls geeignet - der Formel (1a) umfaßt und bei Raumtemperatur flüssig oder leicht schmelzbar ist und im wesentlichen frei von Lösungsmitteln ist, in Abwesenheit oder Gegenwart eines weiteren Vinylcomonomers und/oder Photoinitiators in eine Form,

20 (b) Induzieren der Photovernetzung und

(c) Öffnen der Form, so daß das Formteil aus der Form entfernt werden kann.

19. Verfahren zur Herstellung eines Formteils, das die folgenden Stufen umfaßt:

25 (a) Herstellen einer im wesentlichen wäßrigen Lösung eines wasserlöslichen Präpolymers, das Struktureinheiten der Formel (1) und - falls geeignet - der Formel (1a) umfaßt, in Abwesenheit oder Gegenwart eines weiteren Vinylcomonomers und/oder Photoinitiators,

(b) Einbringen der erhaltenen Lösung in eine Form,

(c) Induzieren der Vernetzung und

(d) Öffnen der Form, so daß das Formteil aus der Form entfernt werden kann.

30

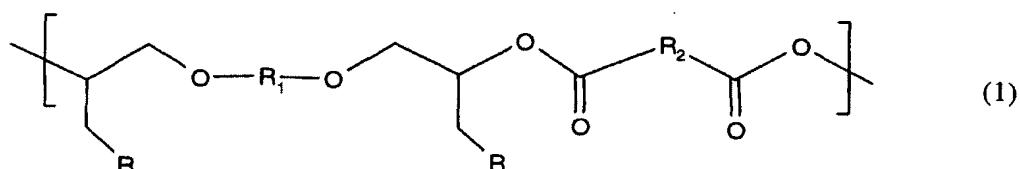
20. Verfahren nach einem der Ansprüche 18 oder 19, wobei das Formteil eine Kontaktlinse ist.

21. Formteil, insbesondere eine Kontaktlinse, erhältlich nach dem Verfahren gemäß Anspruch 18 oder 19.

35 22. Kontaktlinse nach Anspruch 21, die sich für ihre vorgesehene Verwendung ohne Extraktion eignet.

Revendications

40 1. Un prépolymère comprenant des unités structurelles de formule

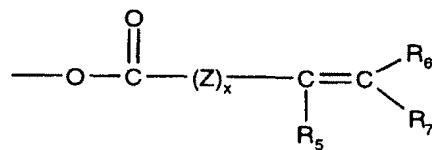


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où R est un radical

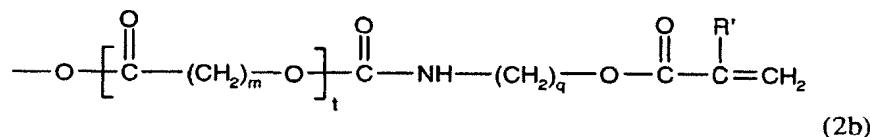
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EP 0 932 635 B1



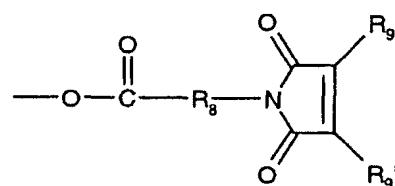
(2a),

10



(2b)

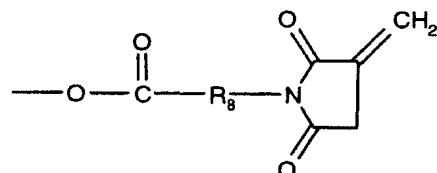
20



(2c)

ou

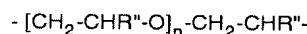
30



(2d),

40 Z signifie un groupe C₁-C₁₂alkylène à chaîne droite ou ramifiée ou un groupe phénylène ou C₇-C₁₂aralkylène non substitué ou C₁-C₄alkyl- ou C₁-C₄alcoxy-substitué,
 x et t signifient chacun indépendamment de l'autre, le nombre 0 ou 1,
 R₅ signifie l'hydrogène, un groupe C₁-C₄alkyle ou un halogène,
 R₆ signifie l'hydrogène, un groupe C₁-C₄alkyle, phényle, carboxy ou un halogène,
 R₇ signifie l'hydrogène lorsque R₆ signifie un groupe phényle ou carboxy, ou bien signifie l'hydrogène ou un groupe carboxy lorsque R₆ signifie l'hydrogène, un groupe C₁-C₄alkyle ou un halogène,
 R₈ signifie un radical C₂-C₁₂alkylène, un radical phénylène ou un radical C₇-C₁₂aralkylène,
 R₉ et R₉' signifient chacun indépendamment de l'autre, l'hydrogène, un groupe C₁-C₄alkyle ou un halogène,
 R₁ signifie un radical de formule

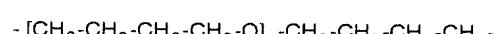
50



(3a)

55

ou



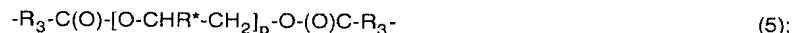
(3b);

EP 0 932 635 B1

ou un radical alkylène ayant jusqu'à 20 atomes de carbone qui peut être interrompu par un ou plusieurs groupes ester, uréthane ou uréido et/ou peut être substitué par un groupe hydroxy ; ou un radical cycloalkylène ayant de 6 à 20 atomes de carbone ; ou un radical arylène ayant de 6 à 20 atomes de carbone ; ou un radical arylènealkylène, alkylènearylène, alkylènearylènealkylène ou arylènealkylènearylène,
 5 R_2 signifie un radical de formule



10 ou



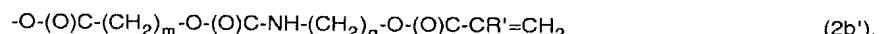
15 ou un radical alkylène ayant jusqu'à 20 atomes de carbone qui peut être interrompu par un ou plusieurs groupes ester, uréthane ou uréido et/ou peut être substitué par un groupe hydroxy ; ou un radical cycloalkylène ayant de 6 à 20 atomes de carbone ; ou un radical arylène ayant de 6 à 20 atomes de carbone ; ou un radical arylènealkylène, alkylènearylène, alkylènearylènealkylène ou arylènealkylènearylène,
 20 R' , R'' et R^* signifient chacun indépendamment des autres, l'hydrogène ou un groupe $C_1\text{-}C_4$ alkyle,
 R_3 signifie un radical alkylène ayant jusqu'à 20 atomes de carbone ; ou bien un radical cycloalkylène ayant de 6 à 20 atomes de carbone ; ou bien un radical arylène ayant de 6 à 20 atomes de carbone, et
 n, m, p et q signifient chacun indépendamment des autres, un nombre de 1 à 30,

25 au moins un des radicaux R_1 et R_2 devant signifier un radical de formule (3a), (3b), (4) ou (5).

2. Un prépolymère selon la revendication 1, où R signifie un radical de formule



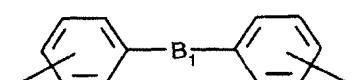
30 ou



35 R_5 et R' signifient chacun indépendamment de l'autre, l'hydrogène ou un groupe $C_1\text{-}C_4$ alkyle, et m et q signifient chacun indépendamment de l'autre un nombre de 1 à 30.

40 3. Un prépolymère selon la revendication 2, où R signifie un radical de formule (2a') où R_5 signifie l'hydrogène ou un groupe méthyle.

45 4. Un prépolymère selon l'une quelconque des revendications 1 à 3, où R_1 signifie un radical de formule (3a) ou (3b) indiqué à la revendication 1, un groupe $C_1\text{-}C_{20}$ alkylène, 1,2-, 1,3- ou 1,4-phénylène, ou un radical de formule

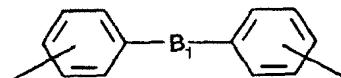


50 où B_1 signifie un groupe $C_1\text{-}C_4$ alkylène à chaîne droite ou ramifiée.

55 5. Un prépolymère selon l'une quelconque des revendications 1 à 4, où R_1 signifie un radical de formule (3a) indiqué à la revendication 1, ou signifie un groupe $C_1\text{-}C_{20}$ alkylène.

6. Un prépolymère selon l'une quelconque des revendications 1 à 5, où R_2 signifie un radical de formule (4) ou (5) indiqué à la revendication 1, un groupe $C_1\text{-}C_{20}$ alkylène, 1,2-, 1,3- ou 1,4-phénylène, ou un radical de formule

EP 0 932 635 B1



5

où B₁ signifie un groupe C₁-C₄alkylène à chaîne droite ou ramifiée.

10

7. Un prépolymère selon l'une quelconque des revendications 1 à 6, où R₂ signifie un radical de formule (4) indiqué à la revendication 1, ou signifie un groupe C₁-C₂₀alkylène.

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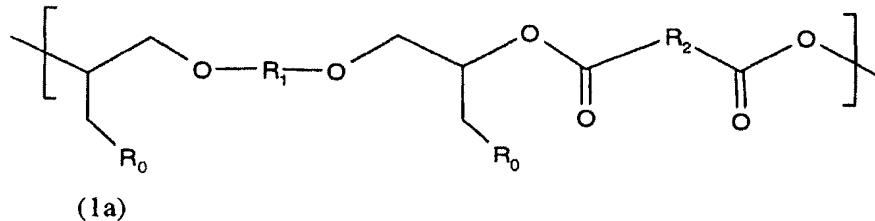
8. Un prépolymère selon l'une quelconque des revendications 1 à 7, où R₁ signifie un radical de formule (3a) indiqué plus haut et R₂ signifie un radical C₁-C₂₀alkylène.

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9. Un prépolymère selon l'une quelconque des revendications 1 à 7, où R₁ signifie un radical C₁-C₂₀alkylène et R₂ signifie un radical de formule (4) indiqué plus haut.

10. Un prépolymère selon l'une quelconque des revendications 1 à 9 qui comprend, outre des unités structurelles de formule (1), des unités structurelles de formule

25



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où R₀ signifie un halogène ou un radical -O-(O)C-R₄ et R₄ signifie un groupe C₁-C₂₀alkyle, C₆-C₂₀cycloalkylène, C₆-C₂₀arylène ou C₇-C₁₂aralkylène.

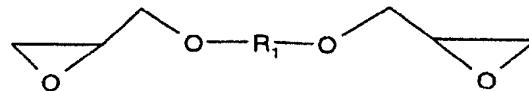
35

11. Un prépolymère selon la revendication 10, où R₀ signifie un halogène, de préférence le chlore.

40

12. Un procédé de préparation d'un prépolymère selon la revendication 1, caractérisé en ce que

a) on polymérisé un composé de formule



(6)

45

avec un composé de formule

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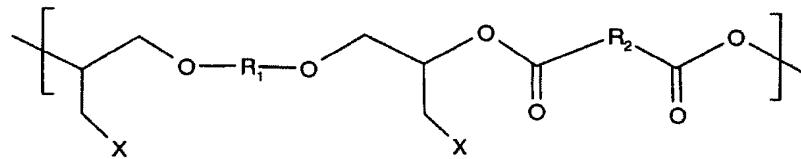
X(O)C-R₂-C(O)X (7)

en présence d'un catalyseur, et

55

(b) on fait réagir le polymère pouvant être obtenu selon (a), qui comprend des unités structurelles de formule

EP 0 932 635 B1



(1a),

10 avec un composé de formule

R-H

(8)

15 en présence d'une base, R_1 et R_2 étant chacun comme défini à la revendication 1, X signifiant un halogène, de préférence le chlore, et R signifiant un radical de formule (2a), (2c), (2d) ou (2b) indiqué à la revendication 1 où t signifie le nombre 1.

20 13. Un polymère qui peut être obtenu par réticulation d'un prépolymère selon l'une quelconque des revendications 1 à 11, en l'absence ou en présence d'un comonomère vinylique supplémentaire.

14. Un polymère selon la revendication 13 qui peut être obtenu par photoréticulation d'un prépolymère selon l'une quelconque des revendications 1 à 11, en l'absence d'un comonomère vinylique supplémentaire.

25 15. Un polymère selon la revendication 13 qui peut être obtenu par photoréticulation d'un prépolymère selon l'une quelconque des revendications 1 à 11, en présence de 0,5 à 80 unités d'un comonomère vinylique supplémentaire par unité de formule (1), spécialement de 1 à 30 unités de comonomère vinylique par unité de formule (1) et plus spécialement de 5 à 20 unités par unité de formule (1).

30 16. Un procédé de préparation d'un polymère selon la revendication 13, qui comprend la photoréticulation d'un prépolymère selon l'une quelconque des revendications 1 à 11, en l'absence ou en présence d'un comonomère vinylique supplémentaire.

35 17. Un procédé selon la revendication 16, où le prépolymère est utilisé sous une forme substantiellement pure.

18. Un procédé de production d'un moulage, qui comprend les étapes suivantes :

40 a) on introduit dans un moule un prépolymère comprenant des unités structurelles de formule (1) et, lorsque cela est approprié, (1a) qui est liquide à la température ambiante ou fond facilement et est substantiellement exempt de solvant, en l'absence ou en présence d'un comonomère vinylique supplémentaire et/ou d'un photoinitiateur,

b) on provoque la photoréticulation,

c) on ouvre le moule, pour pouvoir retirer le moulage du moule.

45 19. Un procédé de production d'un moulage, qui comprend les étapes suivantes :

50 a) on prépare une solution substantiellement aqueuse d'un prépolymère soluble dans l'eau comprenant des unités structurelles de formule (1) et, lorsque cela est approprié, (1a) en l'absence ou en présence d'un comonomère vinylique supplémentaire et/ou d'un photoinitiateur,

b) on introduit la solution résultante dans un moule,

c) on provoque la réticulation,

d) on ouvre le moule, pour pouvoir retirer le moulage du moule.

55 20. Un procédé selon la revendication 18 ou la revendication 19, où le moulage est une lentille de contact.

21. Un moulage, spécialement une lentille de contact que l'on peut obtenir selon le procédé selon la revendication 18 ou la revendication 19.

EP 0 932 635 B1

22. Une lentille de contact selon la revendication 21 qui est appropriée pour son utilisation envisagée, sans extraction.

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